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Abstract

R-curves of single-phase Y- and Ca-containing α -SiAlON ceramics have been measured. They range from flat ones for fine-grain ceramics to pronounced rising ones when large elongated grains are present. The highest toughness measured reached $11.5 \text{ MPa}\cdot\text{m}^{1/2}$ over a crack extension of about $1000 \text{ }\mu\text{m}$.

Comments

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R-Curve Behavior of *In Situ* Toughened α -SiAlON Ceramics

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R-curves of single-phase Y- and Ca-containing α -SiAlON ceramics have been measured. They range from flat ones for fine-grain ceramics to pronounced rising ones when large elongated grains are present. The highest toughness measured reached $11.5 \text{ MPa}\cdot\text{m}^{1/2}$ over a crack extension of about 1000 μm .

I. Introduction

SILICON NITRIDE has two polymorphs,¹ α -Si₃N₄ and β -Si₃N₄. Commercial silicon nitride ceramics are mostly β -Si₃N₄, because they can be processed to obtain elongated grains^{2–4} that provide self-reinforcement.^{5,6} Such *in situ* toughened nitride ceramics have high strength and high toughness and are relatively damage tolerant. The damage tolerance and the high toughness are closely related to their *R*-curve behavior. For example, using double cantilever beam measurements in a β -silicon nitride, Li and Yamanis⁷ reported an *R*-curve that rose from 4 to 10 $\text{MPa}\cdot\text{m}^{1/2}$ over a crack extension of about 1000 μm . Subsequent experiments have confirmed this observation.⁸ It is also known that the properties of β -Si₃N₄ can be further improved by microstructure control using seeding and texturing, effected, for example, by tape casting. Using these methods, Kanzaki *et al.*^{9,10} reported β -Si₃N₄ ceramics with a strength of 1–1.4 GPa and a toughness of 8.5–12 $\text{MPa}\cdot\text{m}^{1/2}$.

Recently, *in situ* toughened α -Si₃N₄ solid solutions (commonly called α -SiAlON¹¹) have been discovered.^{12,13} Like *in situ* toughened β -Si₃N₄, they contain elongated grains and exhibit self-reinforcement. One advantage of α -SiAlON is that they are much harder than β -Si₃N₄ ($H_{V10} = 20$ –22 GPa compared with 15–16 GPa).^{14,15} Therefore, they should be particularly suited for wear-related applications. No *R*-curve for this class of materials, however, has been reported. In this communication, we present our initial studies of *R*-curves of a variety of α -SiAlON ceramics. These results are compared with observations in β -Si₃N₄ and with microstructures.

II. Experimental Procedure

(1) Compositions

The compositions investigated in our experiments lie in the single-phase area of the α -SiAlON plane represented by the formula $\text{M}_{m/z}\text{Si}_{12-(m+n)}\text{Al}_{m+n}\text{O}_n\text{N}_{16-n}$. Here M stands for a

metal interstitial cation that has a valence z . The data are for M = Y, $m = 1.5$, $n = 1.2$ (Y1512); M = Ca, $m = 1.5$, $n = 1.2$ (Ca1512); and M = Ca, $m = 0.8$, $n = 0.9$ (Ca0809).

(2) Powder Preparation

Starting powders of α -Si₃N₄ (SE-E-10, Ube Industry, Ube, Japan), AlN (type F, Tokuyama Soda Co.), Al₂O₃ (AKP50, Sumitomo Chemical America), Y₂O₃ (P3598, ALFA-Johnson Matthey Co.), and CaCO₃ (CS-3NA, Pred Materials, Inc.) were used. The residual oxygen content in α -Si₃N₄ (1.24 wt%) and AlN (0.88 wt%) was taken into account in the composition formulation. The powder mixtures were attrition milled in isopropyl alcohol for 2 h with high-purity Si₃N₄ milling media in a Teflon-coated jar. The powder slurry was subsequently dried in a plastic beaker under a halogen lamp while being stirred.

When desired, charges of seed crystals were added 10–15 min before the end of milling, followed by the same process described above. These seed crystals have compositions matching the final ceramic compositions. Therefore, their only effect is on the microstructure development. The amount of seed crystals used ranged from 0 to 5 wt% for data reported here. Seed crystals were grown from a liquid phase, of an appropriate composition, by annealing it in a nitrogen atmosphere. The liquid/crystal compact was then crushed and subsequently washed in acids to remove the residual phase. The sizes of seed crystals used were 0.3–0.5 μm in width and 1–2.5 μm in length for Y1512, 0.1–0.4 μm and 0.5–1.5 μm for Ca1512, and 0.1–0.3 μm and 0.5–1 μm for Ca0809. Details of the preparation methods for these seeds will be published elsewhere.

(3) Hot Pressing

Powder mixtures were hot-pressed under a uniaxial pressure of 30 MPa in a graphite resistance furnace in a nitrogen atmosphere. Heating rates from 10° to 25°C/min were used. Full densification was observed in all cases. Details of the heat treatment schedule and the amount of seed crystals are listed in Table I.

(4) Characterization

Phase analysis was performed by X-ray diffraction using pulverized samples. In all cases, single-phase α -SiAlON was confirmed. Microstructures of sintered samples were observed on polished and etched sections. Scanning electron microscopy (SEM) was used for microstructure characterization.

(5) R-Curve Measurement

R-curve behavior for propagating cracks was observed *in situ* in four-point bending on bars (approximate dimensions 30 mm \times 4 mm \times 2 mm) cut from the hot-pressed samples. The tensile surface of the bend bar coincided with the hot-pressing plane. A notch of 2 mm, or $\sim 50\%$ of the height of the specimen, was first machined. It was then further notched by another 0.5–1 mm using a tungsten wire (25 μm) saw traveling in a 1 μm diamond paste.

Four-point bending for *R*-curve measurement was performed using a stiff fixture similar to the ones described in the literature.^{16,17} The inner and outer spans were, respectively, 10 and

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Table I. Compositions and Processing Methods of Y- and Ca- α -SiAlON Ceramics

Designation	Composition	Amount of seed (wt%)	Hot-pressing schedule	
			Heating rate (°C/min)	Soak temperature (°C)/Time (h)
Y-1	Y 1512	0	15	1900/1
Y-2	Y 1512	5	15	1900/1
Y-3	Y 1512	1	15	1950/1
Ca-1	Ca 0809	0	10	1800/1
Ca-2	Ca 1512	0	10	1800/1
Ca-3	Ca 1512	4	10	1900/1
Ca-4	Ca 1512	1	10	1950/1

20 mm. The load was applied using a ceramic piezoelectric actuator and measured by an in-line load cell with an accuracy of 0.1 N. (The total load was in the range of 10–200 N.) For *in situ* crack length measurement, a microscope with a long focal length (12 mm at 200 \times) from the objective lens was used. To enhance contrast, an organic fluorescent dye (ZL-37 Zyclo penetrant from Magnaflux) was used in conjunction with a Hg ultraviolet light source. A typical resolution achieved under such condition was ~ 5 μm . Fracture toughness was calculated using the following formula:¹⁸

$$K_{IC} = (\sigma \sqrt{\pi c}) F(\alpha) \quad (1)$$

where

$$\alpha = \frac{c}{w}$$

$$\sigma = \frac{3(s_1 - s_2)P}{2bw^2}$$

$$F(\alpha) = \sqrt{\frac{\tan\left[\left(\frac{\pi}{2}\right)\alpha\right]}{\left(\frac{\pi}{2}\right)\alpha}} \left[\frac{0.923 + 0.199\left\{1 - \sin\left[\left(\frac{\pi}{2}\right)\alpha\right]\right\}^4}{\cos\left[\left(\frac{\pi}{2}\right)\alpha\right]} \right]$$

Here c is the crack length, σ is the net section stress, and F is a geometric factor calculated from the ratio of c and w , which is the height of the bend bar. This formula is accurate for the whole range of c/w with an accuracy of 0.5%. Using the above method, we were able to follow the R -curve to a point very close (within about 25 μm) to the crack initiation. The latter limit was placed by the notch root width, which was about 25 μm .

III. Results and Discussion

R -curves obtained from α -SiAlON vary greatly. They range from ones that are rather flat (Fig. 1(a)), with a relatively low value of fracture toughness (3–5 $\text{MPa}\cdot\text{m}^{1/2}$), to ones that continue to rise

even after 1000 μm of crack propagation (Fig. 1(c)), reaching high values of toughness (>10 $\text{MPa}\cdot\text{m}^{1/2}$). Between these two limits are ones that rise over some considerable distance (from 100 to 700 μm) before an apparent steady-state toughness, ranging from 6 to 10 $\text{MPa}\cdot\text{m}^{1/2}$, is obtained (Fig. 1(b)). The lowest toughness measured in R -curves lies around 3 $\text{MPa}\cdot\text{m}^{1/2}$, which is about the same as the lowest toughness reported for β - Si_3N_4 .¹⁹ This, for example, was obtained in Ca-0809, hot pressed at 1800°C without seeds. The microstructure of this ceramic has very fine, equiaxed grains of 0.5 μm in diameter.

Different α -SiAlON ceramics can be brought to bear different types of R -curves by varying the processing methods. For example, in the case of Y1512, three ceramics processed using the methods listed in Table I exhibit the three types of R -curves mentioned above. Their microstructures, shown in Fig. 2, clearly suggest a strong correlation between coarsening and a rising R -curve with a higher toughness. The highest toughness was obtained when the microstructure is distinctly bimodal, with a high proportion of large, elongated grains, some up to 30 μm long and 5 μm wide (Fig. 2(c)). On the other hand, the lowest toughness with a flat R -curve (5 $\text{MPa}\cdot\text{m}^{1/2}$) was obtained when the grains are small (about 1–2 μm) and mostly equiaxed (Fig. 2(a)). Note that even this relatively low toughness is already higher than the base-line toughness (3 $\text{MPa}\cdot\text{m}^{1/2}$) expected for SiAlON grains (see Fig. 1(a)). Therefore, it is likely that some microstructural toughening also takes place in this microstructure. Indeed, when this Y-SiAlON ceramic was overetched, its microstructure (not shown here) revealed that most grains tend to be slightly elongated, with an aspect ratio of about 2. The very fine microstructure probably causes the R -curve to rise very rapidly, a feature not captured in our measurement because of the finite width of the notch root.

Ceramics of Ca1512 composition show a similar correlation between coarsening and rising R -curves with higher toughness. The processing methods used for these ceramics are also listed in Table I and their microstructures shown in Fig. 3. Note that grains are predominantly elongated even in the finest microstructure. For example, Fig. 3(a) shows a microstructure with needlelike grains with a width of 0.5–1 μm and an aspect ratio of about 5. Yet this microstructure yields a flat R -curve with a toughness of 5 $\text{MPa}\cdot\text{m}^{1/2}$. While some toughening is apparent in this case, β - Si_3N_4 of a comparable microstructure can often reach a higher toughness (6–6.5 $\text{MPa}\cdot\text{m}^{1/2}$).⁹ This would suggest that the grain boundaries in this Ca- α -SiAlON ceramic are relatively strong and crack deflection is relatively difficult. Coarsening of seeded ceramics produces a bimodal grain size distribution, as apparent in Figs. 3(b) and (c). However, the matrix always contains smaller needlelike grains. The largest grains are about 30 μm in length and 4–5 μm in width.

Patterns of crack profiles in these ceramics are consistent with the trend established above. In ceramics that have relatively flat R -curves and low toughness, the crack paths are rather straight. As the R -curve rises and toughness increases, the crack begins to follow a zigzag path. For the toughest ceramics tested here, their

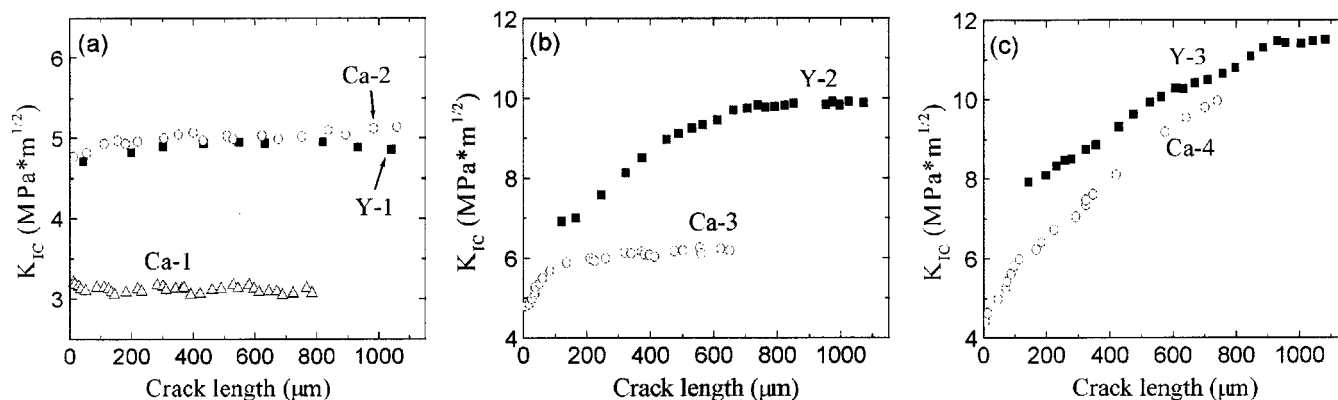


Fig. 1. R -curves of α -SiAlON ceramics. Specimen designations and their processing methods are summarized in Table I.

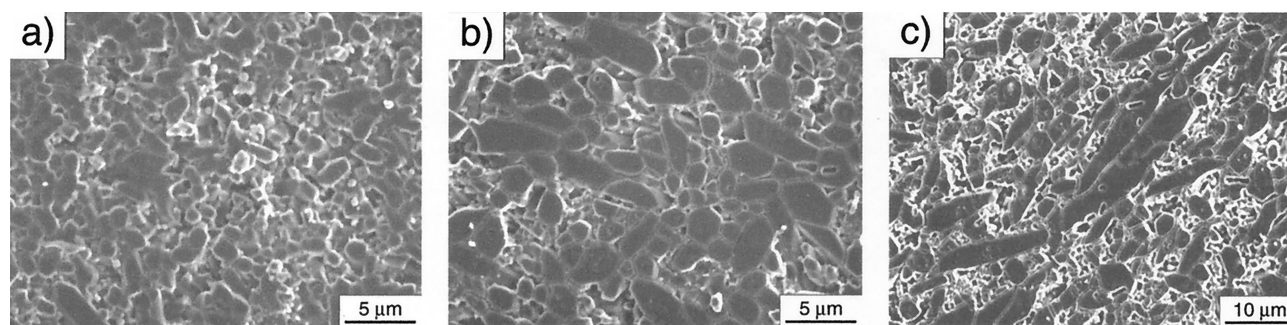


Fig. 2. SEM micrographs showing microstructures of Y1512 ceramics with increasing toughness. They correspond to specimens Y-1 to Y-3 in Table I.

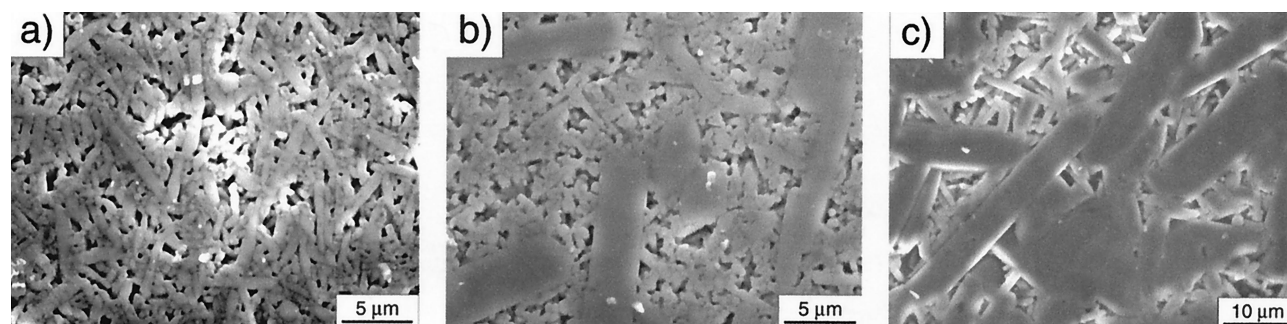


Fig. 3. SEM micrographs showing microstructures of Ca1512 ceramics with increasing toughness. They correspond to specimens Ca-2 to Ca-4 in Table I.

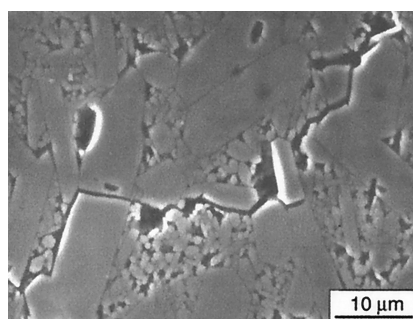


Fig. 4. SEM micrograph of crack showing crack undulation. Sample etched after *R*-curve measurements. It corresponds to specimen Ca-4.

crack paths show undulation with a large amplitude of about 10–15 μm (Fig. 4). In the latter ceramics, cracks often branched off and so severely deviated from the direction of the precrack that the *R*-curve measurements had to be aborted. Subsequent microstructure examinations revealed large grains blocking the crack path, forcing it to detour. It should be mentioned that the different patterns of crack profiles manifest at all stages of propagation, independent of crack lengths. Thus, they are not related to large-scale bridging effects such as the ones described in Refs. 20 and 21.

IV. Conclusions

R-curves of α -SiAlON ceramics have been measured and they show similar features observed in other tough ceramics. The highest toughness is comparable to that of tough β - Si_3N_4 ceramics, and is associated with a bimodal distribution of rodlike grains.

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